WASHINGTON STATE UNIVERSITY
TRI-CITIES

August 14

Dr. Randy Segawa
Agriculture Program Supervisor IV
Environmental Monitoring
California Department of Pesticide Regulation
1001 I Street
Sacramento, CA 95812-4015

Dear Dr. Segawa,

Please find enclosed my review on proposed regulations for fumigant volatile organic compounds together with the signed Attachment 1, "Acknowledgement of Data Handling Responsibilities."

Please feel free to contact me if you have any questions in regard to my review.

Sincerely,

ORIGINAL SIGNED BY

Dr. Vincent R Hebert
Laboratory Research Director
WSU-Food and Environmental Quality Laboratory
509-372-7393

Reviewer:
Dr. Vincent R Hebert
Associate Professor/Department of Entomology
Laboratory Research Director
Washington State University-Food and Environmental Quality Laboratory

I have received the following documentation to aid in my review of the proposed regulations:

1) A summary of the proposed actions (Attachment 1)
2) A description of the scientific issues to be addressed (Attachment 2)
3) Those individuals involved in the proposed fumigant regulations (Attachment 3)
4) The amended text of proposed regulations (28 pages)
5) Initial statement of reasons (ISR) and public report
6) Main references used in the creation of the DPR review document included:
    a. Barry, T. “Methyl Bromide Emission Ratio Groupings”; memorandum, Dec. 2, 1999; Department of Pesticide Regulation, CA.
    b. Barry, T. “Development of Methyl Isothiocyanate Buffer Zones Using the Probabilistic Exposure and Risk Model for Fumigants Version 2 (PERFUM2)”; memorandum, Jan. 27, 2006; Department of Pesticide Regulation, CA.
    c. Barry, T.; Spurlock, F.; Segawa, R. “Pesticide Volatile Organic Compound Emission Adjustments for Field conditions and Estimated Volatile Organic Compound Reductions - Initial Estimates”; DPR memorandum, Apr. 6, 2007
    d. Beard, K.K.; Murphy, P.G.; Fontain, D.D.; Weinberg, J.T. Monitoring of Potential Worker Exposure, Field Flux and Off-Site Air Concentration during Chloropicrin Field Application; Study I.D. HEH 160, 1996; Chloropicrin Manufacturers Task Force, CA. Performed under FIFRA Guideline 133-A-SS. 282 of 701 pages received for this review.
    e. Gan, J.; Yates, S.R.; Spencer, W.F.; Yates, M.V.; Jury, W.A. Atmospheric pollutants and trace gases: Laboratory-scale measurements and simulations of effect of application methds on soil methyl bromide emissions. *J. Environ. Qual.* 26:310-317 (1997).
    f. Johnson, B. Calculation of emission potential factors for 1,3-dichloropropene for five areas for periods from May 1 through October 31. November 30, 2006. DPR memorandium
    g. Knuteson, J.A.; Petty, D.G.; Shurdut, B.A. “Field Volatility of 1,3-Dichloropropene in Salinas Valley California”; Study I.D. ENV91011, 1992; DowElanco, MI. Performed under 40CFR Part 160 Subdivision N Guideline 163-3 Field Volatility. 89 of 130 pages received for this review.
    h. Pilling, R.L. “Carbon Disulfide Flux from Low Volume Emitter Application of Enzone®”; Study No. AA19, 1996; Entek Corp., CA. 107 of 512 pages received for this review.
    i. Rice, P.; White, M.T. “Basamid® (BAS 002 N) Air Monitoring Study in California”; Study No. 158884, 2004; BASF Corp., NC. Performed under 40CFR Part 160 Subdivision N Guideline 163-3 Field Volatility. 45 of 272 pages received for this review.
    j. Rotondaro, A. “Monitoring of Chloropicrin Emissions from Field and Greenhouse Drip Irrigation Applications, and Implied Worker Inhalation Exposure from Field

Applications of Chloropicrin by Shank Injection, Drip Irrigation Systems and at Tree Replant Sites"; Study I.D. PRS02004, 2004; Chloropicrin Manufacturers Task Force, CA. Performed under 40CFR Part 160 OPPTS 875 Series. 121 of 793 pages received for this review.

k. Yates, S.R.; Gan, J.; Ernst, F.F.; Mutziger, A.; Yates, M.V. Methyl bromide emissions from a covered field: I. Experimental conditions and degradation in soil. *J. Environ. Qual.* 25:184-192 (1996).
l. Yates, S.R.; Ernst, F.F.; Gan, J.; Gao, F.; Yates, M.V. Methyl bromide emissions from a covered field: II Volatilization. *J. Environ. Qual.* 25:192-202 (1996).

Besides the memoranda, academic peer reviewed literature, and regulatory science documents provided by DPR, Appendix A includes information I relied upon for the construction of this review. As per the DPR memorandum (Gosselin, 2007; Appendix A) I have also attached a brief CV (Appendix B) listing my capability in responding to issues regarding field fumigation, environmental modeling, and atmospheric chemistry. The main focus of this review is on California's Department of Pesticide Regulation (Cal DPR) adoption of their proposed VOC emission factor estimations.

Areas for Review:

1. Scientific basis for estimation of emission adjustment factors

The Cal DPR information provided by Barry, Spurlock, and Segawa in their memo to John Sanders dated April 6, 2007 thoroughly addresses their rationale for using various adjustments to better estimate fumigant emission factors. As stated in their memo, the VOC tropospheric contribution can be derived by if the pounds of the active ingredient its emission potential can be reasonably established. Additionally, a fumigant –specific application method adjustment factor can be applied to yield a more refined estimate of fumigant VOC contributions within a particular non attainment area(s). Estimations are coupled with incorporating Method Use Fractions (MUFs) as part of the overall VOC emission adjustment. Doing so, in the view of the Barry et al. can lead to the most refined estimates of fumigant VOC emissions in the five non-attainment areas (NAAs) currently under consideration as part of the Clean Air Act.

The refinements used in this memorandum for establishing method adjustment factors principally rely on averaged flux data from "real world" field volatilization information conducted in southern California supplied by registrants as part of 40 CFR Part 160 GLP pesticide registration requirements (chloropricrin, dazomet, 1,3-dichloropropene). The quality and science of the GLP field/laboratory information provided for these field assessments are of the highest standards available for making informed regulatory fumigant emission decisions. However, the studies are few, and understandably not performed in a uniform manner when it comes to controlling climatic conditions, application rates, formulation, soil types, application conditions/equipment/ or seasonal variation.

The Cal DPR memorandum by B. Johnson dated November 30, 2006 provides a clear indication of the assumptions and limitations required for making informed judgments based on the best available science. Here, the researcher is asked to estimate emission potential factors for 1,3-

dichloropropene for five NAAs spanning the ozone period of May through October.
Only two GLP field volatility studies performed at different times and different soil incorporated shanking depths could be used for this assessment. The best available peer-reviewed literature on subsurface flux for 1,3-dichloropropene (Cryer, 2005 and Gan et al. 1998, see Appendix A) must be evaluated by this researcher to come to an informed decision on calculating (linear or non-linear?) emission factors for non-summer and summer conditions for the five NAAs. Obviously, variability in estimation should be anticipated based the various assumptions and limited field studies, thus, estimates in calculated emission potentials should be conservatively weighed.

2. Use of extrapolated method to determine emission factors for methods without data

The work described in the above paragraph uses an interpolation from two field studies to estimate emission potential. I find this acceptable. The memorandum of Barry et al., 2007 unfortunately has to draw upon the available field volatilization studies of certain fumigants to develop more refined emission factors for other fumigant types to account for the effect of application method on May-October VOC emissions. Here, assumptions are made when there is no supportive VOC emission information. Some of these assumptions are based on available application method information that supports the use of a particular fumigation product. For example, various State agency and industry investigators have compiled sprinkler head, drip line, and soil incorporated shank treatments with water sealing for applications of metam sodium. Intermittent watering after either sprinkler head or shank injection has been demonstrated to appreciably reduce surface emission of gaseous methyl isothiocyanates (MITC), presumably by sealing the soil, thus retarding off-gassing, especially during evening hours (see Attachment A, Sullivan citations). Table 22 of Barry's memorandum indicates that a three-fold application reduction factor is applied when water sealing is used in concert with either sprinkler head or shank injection for this product. Barry assumes that chloropicrin and 1,3-dichloropropene soil treatments will also respond similarly and prescribes three fold reductions in fumigant emissions. Although physically it seems plausible, the physicochemical properties are different among these three fumigants. What works for one, could either attenuate or enhance VOC emissions (although unlikely) unless verified through laboratory chamber or better, field flux determinations.

3. Review mitigated fumigant application methods to determine feasibility and alternatives

Incorporating Method Use Fractions (MUFs) as part of the overall VOC emission adjustment is an excellent approach. California is unique in having fairly complete PURs and County Agricultural Commissioners who can work with the grower community in adopting reduced emission technologies to protect the continued use of the fumigant for their crop needs. This addition will greatly aid in making the VOC inventory more accurate. The unfortunate side of this, as stated by Barry et al. 2007, Table 23, low emission methods may not be sufficient in two of the agriculturally important NAAs. Therefore, in my estimation, it may be necessary to examine alternatives such as steps to revise the 1994 Ozone SIP to substitute reactive organic gas (ROG) emission reductions from California's on-going motor vehicle control program for ROG emission reductions in important agricultural counties that must (for the moment) rely on fumigation.

4. The Bigger Picture

My review has been directed so far to address the three questions raised in Attachment 2 concerning the science behind the Barry et al. 2007 memorandum which deals with the Court issued remedy of El *Comité para el Bienestar de Earlimart v. Helliker (2006)* requiring DPR to adopt regulations that will achieve a 20% reduction by January 1, 2008. The fundamental question is whether in the affected non attainment California air basins, if a reduction of 8 tons per day of VOC from current pesticide inventory emission levels of 26 tons per day are realistically achievable though adoption of fumigant emission reduction best management practices. As per Barry et al., 2007 DPR memo, the prospect for near-term VOC emission reductions seems especially problematic for two NAAs, even if the more stringent emission reduction tactics listed in Table 23 are immediately implemented. The 2003 inventory shows that the Ventura NAA had VOC levels nearly double the 1990 baseline, approximately 93% of which are from fumigants. As I stated earlier, it may be necessary to revise the 1994 Ozone SIP to substitute reactive organic gas (ROG) emission reductions from California's on-going motor vehicle control program for ROG emission reductions or immediately face loosing economically important agricultural acreage.

A second area that falls outside of the questions raised in Attachment 2 but I believe require attention is to better understand the reactivity of the individual active ingredients. Under California's 1994 State Implementation Plan (SIP) there are provisions for considering the *reactivity* of the individual compounds. Many of the fumigant VOCs under review have widely divergent maximum incremental reactivities (MIRs) towards formation of ozone (Carter and Malkina, 2007; Appendix A). If the real question is reducing troposphere ozone impacts on human health and plant communities, then the MIR reactivity for each of these high use fumigants should also be better understood in regional context. Unfortunately, based on the excellent work of Carter and Malkina, certain agriculturally fumigants will fair well while others will not if ozone formation potential rather than VOC emissions are considered as part of an overall pollutant emissions factor.

A third area that understandably falls outside the first three questions raised in Attachment 2 is the significance of biogenic VOC source contributions and their potential impacts on ozone levels in California basin NAAs. Based on experimental measurements, the biogenic hydrocarbons from many urban vegetative sources can be significantly more reactive in ozone formation than a typical mix of anthropogenic hydrocarbons (Benjamin and Winer, 1998). As these authors state that certain tree species contribute to ozone formation in airsheds polluted with oxides of nitrogen, the important aesthetic and practical benefits for trees and shrubs to remove pollutant gases and particles improving air quality out weigh the need for reducing these VOC source contributions. Similarly, benefits of fumigant use for the food supply and human health should also be carefully considered when developing reduced source emission tactics.

In ending, I wish to commend Cal DPR in their amalgamation of air resources experts from both Cal DPR and Cal ARB together with the group of academic and federal agency consultants who contributed in the development the text for the proposed regulations of fumigant volatile emission compounds.

APPENDIX A: DOCUMENTS RELIED UPON FOR THE CONSTRUCTION OF THIS REVIEW

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Appendix B:

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Research/Extension Emphasis (Year 2000 to present)

I have a long-standing interest and professional involvement in understanding the environmental fate and transport of trace-level organics in air. Our current area of research focuses on administration over a regional ambient air monitoring program for understanding implications of off-target pesticide movement on public health and crop injury. Other areas of active research include: 1) developing analytical methods for assessing specific biomarkers useful for monitoring pesticide exposures to sensitive subpopulations in agricultural communities, 2) the development of field air -sampling methods and volatilization chamber system design for assessing fumigants, pesticides, and semiochemicals useful in codling moth mating disruption, 3) characterizing/isolating bioactive plant volatile emissions from insect herbivory that may prove useful in enhancing conservation biological control in cropping systems, and 4) chemically assessing sublethal concentrations of pesticides in surface waters that can have neurobehavioral effects on salmonids.

A principle responsibility of my appointment is to administer over a state-mandated food and environmental regulatory science facility that conducts studies under federal 40CFR Part 160 Good Laboratory Practices (GLP). This program houses an independent quality assurance unit and GLP Laboratory Coordinator to assure federal compliance.

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- Hebert VR*. Regional off-target movement of auxin-type herbicides. Proceedings of the *International Conference on Pesticide Application for Drift Management*, Kona, Hawaii. 178-183. October 27, 2004.

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